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STUDIES ON TRANSITION METAL PARACYCLOPHANE COMPOUNDS. REACTIONS OF $[\{M(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ $\{M = Ru, Os\}$ WITH TERTIARY PHOSPHINES: THE CRYSTAL STRUCTURES OF $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]\cdot CHCl_3$ AND $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]\cdot 2CH_2Cl_2$

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Abstract—The synthesis of the compound $[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ is described. The reactions of the compounds $[\{M(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (M = Ru, Os) with tertiary phosphines are investigated in polar and non-polar solvents. Neutral compounds $[M(\eta^6\text{-}C_{16}H_{16})Cl_2(PR_3)]$ and cationic complexes $[M(\eta^6\text{-}C_{16}H_{16})Cl(PR_3)_2]^+X^-$ ($X = PF_6$, BPh_4) are obtained, respectively. The crystal structure of a representative compound $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$ has been determined and the structure is compared with that of the simpler analogue $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$.

We have previously reported the preliminary results of our investigations into the reactivity of the dinuclear compound $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (**1**) with Lewis bases.[1] We have extended the work to osmium via the compound $[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (**2**), the synthesis and characterization of which we report for the first time. The compounds $[\{M(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (M = Ru, Os) react with a variety of tertiary phosphines (L) in both non-polar and polar solvents, giving monomeric neutral, $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2L]$, and cationic, $[Ru(\eta^6\text{-}C_{16}H_{16})ClL_2]^+$, species respectively. One of the neutral compounds, namely $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$ (**3**) has been characterized by X-ray crystallography as the monochloroform solvate. For comparative purposes we have also determined the structure of $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$ (**4**), as the bis-dichloromethane solvate.

RESULTS AND DISCUSSION

$[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$

The synthetic method used to prepare $[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (**2**) was based on that for **1**.[2] Surprisingly, it proved less tedious and gave higher yields than for the ruthenium analogue. The reverse observation is more frequently made for related pairs of η^6-arene compounds.[3–5] In the first stage of the synthesis, $[Os(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ is reduced using Red–Al. After water is added to destroy the excess reducing agent, the sticky, black residue that forms coagulates and falls to the bottom of the reaction vessel, leaving a clear yellow solution of the desired intermediate $[Os^0(\eta^4\text{-}$

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$C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$. The yellow solution is simply filtered off without the need for the tedious extraction procedure required for **1**, pumped to dryness and treated with a solution of HCl (12 M) in acetone. Compound **2** then readily precipitates as a tan coloured solid. Typical yields were *ca* 75%, which is considerably greater than those obtained for **1** (35–50%), and contamination with the free paracyclophane was also rather less severe. The full synthetic method and spectroscopic and analytical data are presented in the Experimental section.

The ^1H NMR spectrum of **2**, recorded in DMSO-d_6, mirrors that of **1**, with the only significant difference being that the signal due to the coordinated ring protons of the cyclophane ligand appears 0.3 ppm to higher frequency in the osmium complex. This chemical shift difference is comparable in magnitude to that observed for the benzene proton resonances in the complexes $[\{M(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ (M = Ru: δ 5.98; M = Os: 6.15 ppm).[7–9] The ^{13}C NMR spectrum, recorded in DMSO-d_6, is similar to that recorded for **1**. The only noteworthy difference is the additional shift to lower frequencies of the resonances associated with the metal-coordinated carbon atoms. Similar observations have been made for the complexes $[\{M(\eta^6\text{-}C_6H_6)Cl_2\}_2]$.[7–9]

Neutral compounds

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$. Complex **1** was stirred in toluene with an excess of triphenylphosphine at room temperature. The reaction mixture first became yellow and then an orange powder was deposited. The orange powder was isolated by filtration. Microanalytical data closely fitted those expected for $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$ (**3**). In the FAB mass spectrum the molecular ion was observed at 642 mass units (based on the isotopes ^{102}Ru and ^{35}Cl). Fragmentation peaks were observed at 607 and 572 mass units, and indicate the successive loss of the two chloride ligands. The IR spectrum exhibits two terminal ν(Ru—Cl) stretching bands at 281 and 303 cm^{-1}. The ^1H NMR spectrum, recorded in $CDCl_3$, exhibits four resonances due to the coordinated cyclophane ligand: a singlet at δ 6.69 (4H) arising from the non-coordinated aromatic ring protons, a doublet at δ 4.70 (4H, $^3J_{P,H}$ = 1.1 Hz), due to the coordinated aromatic ring protons, and two six-line multiplets at δ 2.31 and 3.01 ppm (each 4H) arising from the methylenic protons. Small (*ca* 1 Hz) three-bond couplings between the protons of coordinated aromatic ligands and the phosphorus-31 nuclei of coordinated tertiary phosphines have been observed previously in related systems.[10] The phenyl protons of the tertiary phosphine ligand give rise to two multiplets at δ 7.32 (9H) and 7.54 (6H) ppm. Integration of the spectrum supports the proposed formulation. A computer-aided spin simulation of the multiplet resonances arising from the $—CH_2CH_2—$ protons of the cyclophane has confirmed the coupling pattern as being of the AA′XX′ type (Fig. 1). The pattern is observed because of the chemical inequivalence of the protons closer to the metal atom (Fig. 2; H_A and $H_{A'}$) compared with those

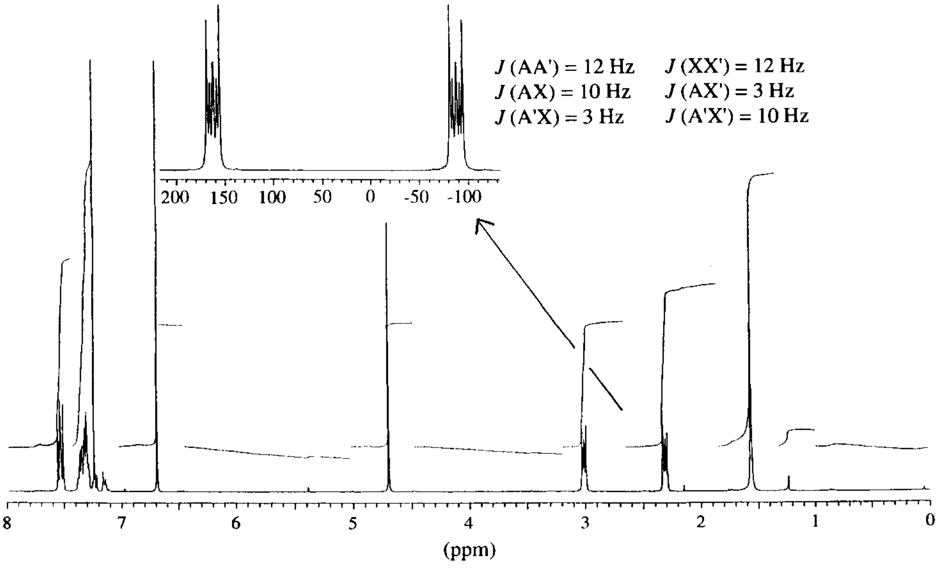

Fig. 1. ^1H NMR spectrum of **3**, recorded at 400 MHz in $CDCl_3$ at 298 K. Inset is the computer-aided spin simulation with derived coupling constants, for the AA′XX′ coupled resonances of the ethylenic protons in the cyclophane ligand.

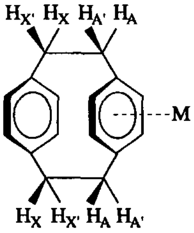

Fig. 2. The appearance of the AA′XX′ coupling pattern in the ^{1}H NMR spectra of species containing an η^6-coordinated [2,2](1,4)cyclophane ligand is governed by (i) the chemical shift difference between protons $H_A/H_{A'}$ and $H_X/H_{X'}$, and (ii) the degree of twist in the ethylenic bridges.

closer to the non-coordinated aromatic deck (H_X and $H_{X'}$) and the fact that the coupling constants are modified by the degree of torsion in the bridging functions. The precise appearance of the coupling pattern is governed by the magnitude of that chemical shift difference and by the torsion angle in the bridging ethylenic functionalities. These resonances had previously been reported only as "multiplets", at a mean chemical shift, which belies the true complexity of the factors governing their appearance.[2,11]

The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a singlet resonance at δ 37.3 ppm arising from the single phosphorus atom of the triphenyl phosphine ligand. A comparable chemical shift of δ 31.6 ppm was reported for the compound $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}Cl)_2(PPh_3)_2][PF_6]_2$.[10]

$[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$. The compound $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$ (**4**) was prepared similarly to **3**. Its synthesis has been reported before via a similar method.[5] Satisfactory analysis figures have been obtained.

Crystallography. The structures of **3** and **4** have been unequivocally confirmed by single-crystal X-ray diffraction experiments. The crystals used for the experiments were obtained by the slow evaporation of chloroform and dichloromethane solutions of the complexes **3** and **4**, respectively. The asymmetric unit of **3** comprises one molecule of the metal complex and one molecule of chloroform, though there are no short contacts between them. For **4**, two molecules of dichloromethane are present together with the metal complex in the asymmetric unit, again with no unusually close intermolecular contacts. The molecular structures of **3** and **4** are presented in Figs 3 and 4. Crystallographic data and selected bond lengths and bond angles appear in Tables 1–3. Details of the data collections and structure refinements are given in the Experimental section.

The geometry at the metal ion of **3** is that of a distorted tetrahedron, with the cyclophane and the other ligands adopting a "piano-stool" configuration. The arene adopts a staggered conformation with respect to the other three ligands, and is therefore similar to the structures of the complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PMePh_2)]$ and $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PMePh_2)]$.[12] The angles between non-cyclophane ligands are all close to 90°, and are typical for structures of this type.[12–14] The C—P—C angles about the phosphorus atom fall in the range 101–106°, while the Ru—P—C angles are in the range 108–122°. Thus, the geometry at the phosphorus atom is distorted from being an ideal tetrahedron by the phenyl rings being displaced away from the metal centre. Several reported related structures also exhibit this distortion.[15,16] The phenyl rings of the PPh_3 ligand show no significant deviation from planarity. The Ru—Cl distances are 2.383(1) and 2.392(2) Å, and are therefore slightly shorter than those typically observed, which lie in the range 2.39–2.42 Å.[12,14,16–22] The Ru—P bond length of 2.293(1) Å is unremarkable (Ru—P distances typically fall in the range 2.26–2.35 Å[12,15,16,19,21,23,24]).

As has been observed in previously reported[1,6,13,25,26] structures containing a metal-coordinated cyclophane ligand, there are two long [2.299(4) and 2.381(5) Å] and four short [av. 2.19(1) Å] Ru—C bonds. This irregularity arises from the shallow boat conformation of the aromatic cyclophane decks. In this compound there is an additional distortion present whereby the Ru—C bonds *trans* to the phosphorus atom are elongated relative to those that are *trans* to the chloride ions. For example, Ru(1)—C(4) (*trans* to P) = 2.38(1) Å, while Ru(1)—C(1) (*trans* to Cl) = 2.30(1) Å; and Ru(1)—C(5) (*trans* to P) = 2.28(1) Å, while Ru(1)—C(2),(3),(6) (*trans* to Cl) = *ca* 2.16(1) Å. Similar observations were made for the complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PMePh_2)]$ and $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PMePh_2)]$ and were attributed to the *trans*-bond-lengthening effect of the tertiary phosphine ligand.[12] In these complexes the arene rings were distorted from planarity rather than simply tilted. Bennett *et al.*[12] argue that this effect would only be possible if there was a significant localization of the π-electron density in the rings, although no C—C bond length alternation was reported for the coordinated aromatic rings. There is substantial evidence for the localization of π-electron density in the coordinated ring of the cyclophane complex **3**. As observed for the chromium complexes $[Cr(\eta^6\text{-}C_{16}H_{16})(CO)_3]$ (**5**) and $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$,[27] and also for the ruthenium complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(2\text{-hydroxypyridine})]$,[18] there is a clear alternation of long [av. 1.41(1) Å]

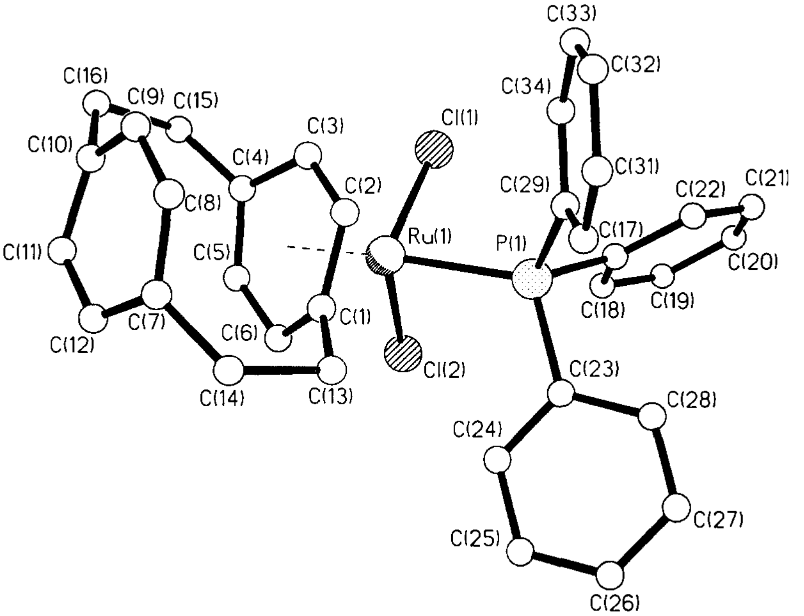

Fig. 3. The molecular structure of **3** with the atomic labelling scheme defined. Hydrogen atoms and the chloroform molecule of crystallization are omitted for clarity.

and short [av. 1.38(1) Å] C—C bond lengths in the coordinated ring. No such bond length alternation is observed in the non-coordinated deck. The distance from the ruthenium ion to the centroid of the non-bridgehead carbon atoms of the coordinated ring [C(2),C(3),C(5),C(6)] is 1.70 Å. This value is comparable to many reported ruthenium–arene distances (typical range: 1.64–1.79 Å[15,17,19,20,22,28–32]).

The cyclophane inter-ring separation, 2.97 Å, shows a decrease of 0.08 Å when compared with the free ligand.[33] The effect is slightly larger in this complex of Ru^{II} than in **5**, where a 0.07 Å shortening was observed.[13] As a result of this contraction the rings flatten slightly, the coordinated face to a greater extent than the non-coordinated one, and the angular distortions for the spacer groups become less severe. The two decks of the cyclophane are not exactly eclipsed (Fig. 5), with torsion angles of 9.9 and 9.7° present in the two ethylenic bridges. The torsion angle in the free ligand is calculated to be much smaller, of the order of 3.2°, while a torsion angle of 3.8° was observed in the structure of complex **5**.[13]

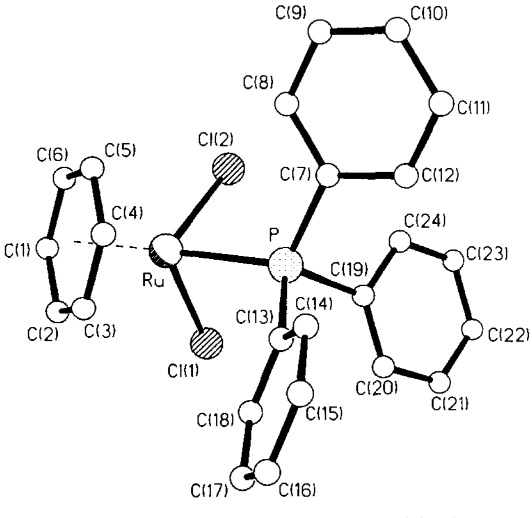

Fig. 4. The molecular structure of **4** with the atomic labelling scheme defined. Hydrogen atoms and the two dichloromethane molecules of crystallization are omitted for clarity.

Compound **4** also adopts a "piano-stool" configuration, but in contrast to **3**, the phosphorus and chlorine atoms eclipse three of the carbon atoms of the η^6-C_6H_6 ring. The angles between the non-benzene ligands are somewhat smaller than those observed for **3** (see Table 3). The geometry at the phosphorus atom is similar to that in **3**. The Ru—Cl distances, Ru—Cl(1) = 2.406(2) and Ru—Cl(2) = 2.412(1) Å, are rather longer than those in the cyclophane analogue, while the Ru—P distance, at 2.364(1) Å, is considerably longer than was observed in **3**.

Whereas two carbon atoms of the cyclophane ligand were *trans* to the phosphorus atom in **3**, and therefore had unusually long Ru—C distances, only C(1) lies directly *trans* to the phosphorus atom in **4**. The *trans*-bond-lengthening effect is again in evidence, however, with Ru—C(1) = 2.23(1) Å being longer than any of the other Ru—C distances [av.

Table 1. Crystallographic and structure solution data for **3** and **4**

Compound formula	$C_{35}H_{32}Cl_5PRu$ (**3**)	$C_{26}H_{25}Cl_6PRu$ (**4**)
M_r	761.9	682.2
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Crystal size (mm)	0.50 × 0.20 × 0.10	0.43 × 0.38 × 0.35
T (K)	293	160
a (Å)	40.325(24)	11.262(6)
b (Å)	8.341(2)	8.217(3)
c (Å)	22.646(7)	29.390(10)
β (°)	120.12(3)	91.86(6)
V (Å^3)	6587(4)	2718(2)
Z	8	4
D_{calc} (g cm^{-3})	1.54	1.67
F(000)	3088	1368
μ (Mo-K_α) (mm^{-1})	0.892	1.241
Orientation reflections, no.; range (2θ)	49; $25° < 2\theta < 35°$	31; $23° < 2\theta < 25°$
Data collection method	ω-scans	ω–θ scans with on-line profile fitting[39]
2θ range (°)	5–55	5–50
h, k, l ranges	0–48 0–10 −27–27	−13–13 −9–9 −34–34
Data measured	6331	7132
No. of unique data	5804	4785
No. of data with $I > 2\sigma(I)$	4413	4502
Refinement method	full-matrix least-squares on F	full-matrix least-squares on F^2
No. of parameters	379	308
Weighting scheme/parameters	$w^{-1} = \sigma^2F + 0.0000264F^2$	see text, $a = 0.0286$, $b = 3.6145$
$R1$ [$I > 2\sigma(I)$]	0.0473	0.0242
R_w	0.0377	—
R_w2 (all data)	—	0.0664
Goodness of fit	1.940 (on F)	1.080 (on F^2)
Extinction coefficient	—	0.011(2)
Largest shift/e.s.d., final cycle	0.035	0.001
Largest peak in difference map (e Å^{-3})	0.48	0.75

2.20(1) Å]. It is noteworthy that the η^6-C_6H_6 ligand is tilted, with C(1) being furthest from the ruthenium atom, and C(4) being closest [2.23(1) vs. 2.17(1) Å], while the ring is essentially planar. The maximum and mean deviations from the mean plane of the six carbon atoms are 0.0123 and 0.0069 Å, respectively. Bennett *et al.*[12] reported that the coordinated arene ligands in the related compounds [Ru(η^6-*p*-cymene)Cl_2($PMePh_2$)] and [Ru(η^6-C_6H_6)Cl_2($PMePh_2$)] were actually distorted from planarity, but this is clearly not the case for **4**. Evidence of bond length alternation around the coordinated ring is less persuasive than it was for **3**, with the three longer lengths averaging 1.41(1) Å, and the three shorter ones averaging 1.39(1) Å. The ruthenium to η^6-C_6H_6 ring centroid distance is 1.70 Å, and therefore typical among similar reported distances, and equal to the value seen in the structure of **3**.[15,17,19,20,28–32]

[Ru(η^6-$C_{16}H_{16}$)Cl_2($PMePh_2$)]. The complex [Ru(η^6-$C_{16}H_{16}$)Cl_2($PMePh_2$)] (**6**) was prepared in an analogous manner to **3**, and has been similarly characterized.

[Os(η^6-$C_{16}H_{16}$)Cl_2(PMe_2Ph)]. The compound [Os(η^6-$C_{16}H_{16}$)Cl_2(PMe_2Ph)] (**7**) was prepared and characterized in a similar fashion to **3**. The ^{1}H NMR spectrum is similar to that of **6**, the only significant difference being that the resonances due

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]\cdot CHCl_3$ (**3**)

Ru(1)—P(1)	2.293(1)	Ru(1)—Cl(1)	2.383(1)
Ru(1)—Cl(2)	2.392(2)	Ru(1)—C(1)	2.299(4)
Ru(1)—C(2)	2.159(5)	Ru(1)—C(3)	2.129(7)
Ru(1)—C(4)	2.381(5)	Ru(1)—C(5)	2.279(4)
Ru(1)—C(6)	2.179(4)	P(1)—C(17)	1.823(4)
P(1)—C(23)	1.814(6)	P(1)—C(29)	1.821(5)
C(1)—C(2)	1.406(8)	C(1)—C(6)	1.383(6)
C(1)—C(13)	1.498(7)	C(2)—C(3)	1.388(8)
C(3)—C(4)	1.421(6)	C(4)—C(5)	1.371(9)
C(4)—C(15)	1.485(9)	C(5)—C(6)	1.406(7)
C(7)—C(8)	1.371(10)	C(7)—C(12)	1.372(6)
C(7)—C(14)	1.491(9)	C(8)—C(9)	1.370(10)
C(9)—C(10)	1.376(10)	C(10)—C(11)	1.385(14)
C(10)—C(16)	1.481(11)	C(11)—C(12)	1.377(10)
C(13)—C(14)	1.567(7)	C(15)—C(16)	1.562(10)
P(1)—Ru(1)—Cl(1)	87.7(1)	P(1)—Ru(1)—Cl(2)	89.1(1)
Cl(1)—Ru(1)—Cl(2)	89.0(1)		

Table 3. Selected bond lengths (Å) and bond angles (°) for $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]\cdot 2CH_2Cl_2$ (**4**)

Ru—P	2.3637(12)	Ru—Cl(1)	2.406(2)
Ru—Cl(2)	2.4118(10)	Ru—C(1)	2.228(3)
Ru—C(2)	2.193(3)	Ru—C(3)	2.201(3)
Ru—C(4)	2.172(3)	Ru—C(5)	2.203(3)
Ru—C(6)	2.214(3)	P—C(7)	1.831(2)
P—C(19)	1.834(2)	P—C(13)	1.835(2)
C(1)—C(2)	1.408(5)	C(1)—C(6)	1.400(6)
C(2)—C(3)	1.380(4)	C(3)—C(4)	1.400(4)
C(4)—C(5)	1.382(5)	C(5)—C(6)	1.407(6)
Cl(1)—Ru—P	86.15(4)	Cl(2)—Ru—P	86.15(4)
Cl(2)—Ru—Cl(1)	88.18(3)		

to the protons of the coordinated cyclophane ring appear at higher frequency in the spectrum of the osmium compound (see Experimental section).

Electrochemistry. Complexes **3** and **6** have been studied electrochemically in dichloromethane solution (0.1 M $TBABF_4$ supporting electrolyte) by cyclic voltammetry. For **3** a fully reversible one-electron oxidation is observed at +1.15 V (relative to Ag/AgCl). The peak-to-peak separation ($\Delta E_p = 60$ mV, at $v = 100$ mV s^{-1}) is characteristic of a one-electron process, while $I_{pa}/I_{pc} \approx 1$. ΔE_p did not change with scan rate in the range 50–500 mV s^{-1}. There is evidence of an irreversible reduction at *ca* −1.35 V. Complex **6** undergoes a reversible one-electron oxidation at +1.08 V ($\Delta E_p = 65$ mV and was constant with the scan rate, $I_{pa}/I_{pc} \approx 1$). The oxidation of **6** occurs at a slightly less positive potential than that for **3**, due to the better electron-releasing properties of the substituent groups on the dimethylphenylphosphine ligand. These results are unusual since, in general, (η^6-arene) ruthenium(II) compounds exhibit only irreversible oxidation behaviour, often resulting in loss of the arene ligand.[18,34]

Ionic compounds

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)_2][PF_6]$. The details of the synthesis of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)_2][PF_6]$ (**8**), and the data used in characterization are presented in the Experimental section. There are two noteworthy features of the ^1H NMR spectrum of **8**. Firstly, the resonance due to the coordinated ring protons of the cyclophane was broadened, but not resolved into a triplet. This is in contrast to the observation made for **3**, where the corresponding

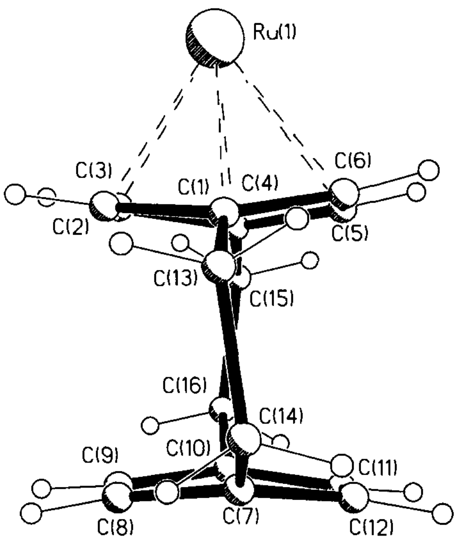

Fig. 5. The $[Ru(\eta^6\text{-}C_{16}H_{16})]$ fragment in the structure of **3** showing the twist in the ethylenic bridging functionalities of the cyclophane ligand.

resonance was split into a doublet by coupling to a single phosphorus atom. Secondly, the two branches of the AA′XX′ coupling pattern arising from the $—CH_2CH_2—$ bridge protons occur at very different chemical shifts (*ca* 1.3 ppm apart). Indeed, this separation is the largest measured for any compound in this study and is undoubtedly due to the presence of two tertiary phosphine ligands in the cation. For the compounds $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2L]$ the largest such separations (*ca* 0.7 ppm) were observed for those compounds containing a tertiary phosphine ligand. The $^{31}P\{^1H\}$ NMR spectrum was recorded in CD_2Cl_2 and exhibits a singlet resonance at δ 26.8 ppm.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2]X$ ($X = [PF_6], [BPh_4]$). The compounds $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)2][PF_6]$ (**9**) and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2][BPh_4]$ (**10**) were prepared and characterized similarly to **8** (see Experimental section).

EXPERIMENTAL

Instrumentation and physical measurements

Elemental analyses were performed by the microanalytical service of the Chemistry Department, University College London. IR spectra were recorded in the region 4000–250 cm^{-1} on a Perkin–Elmer 983 grating spectrophotometer using Nujol mulls on caesium iodide plates. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on either Varian XL-200 or VXR-400 spectrometers. Cyclic voltammetric studies were performed using a Metrohm potentiostat and VA scanner, linked to a cell stand having a three-electrode geometry. The working electrode was a platinum wire. The reference electrode was a non-aqueous $Ag/AgCl/Cl^-$, CH_2Cl_2 electrode, and the auxiliary electrode was a large platinum wire. FAB mass spectra were recorded by the University of London Mass Spectrometry Service at the School of Pharmacy. Computer simulations were used to verify assignments.

Materials

Ruthenium trichloride was activated before use by repeated evaporation of its aqueous solution.[26] $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$, $[\{Os(\eta^6\text{-}C_6H_6)Cl_2\}_2]$, $[Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ and $[Os(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ were prepared by published methods.[4–6,35] All reactions were carried out under dinitrogen in degassed solvents. Tetrahydrofuran and n-hexane were dried before use by distilling from sodium wire. Dichloromethane used for electrochemical studies was distilled from P_4O_{10}. All other reagents and solvents were used as obtained from commercial suppliers.

Synthesis

$[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (**2**). A solution of sodium bis(methoxyethoxy)aluminium hydride (3.4 M) in toluene (1.50 cm^3; 5.10 mmol) was added to a suspension of $[Os(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ (0.86 g; 1.33 mmol) in degassed THF (50 cm^3) at 0°C. After stirring for a few minutes, the solution became a clear, dark amber colour. The solution was stirred for 2.5 h. Water (1.00 cm^3) was added dropwise to destroy the excess reducing agent. The solution, which darkened and formed a sticky dark residue, was stirred for 45 min. During this time the dark residue coagulated and fell to the bottom of the Schlenk tube. The clear, deep yellow solution of $[Os^0(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ was decanted off, filtered and pumped to dryness. The resulting yellow solid was treated with a solution of concentrated hydrochloric acid (2.00 cm^3) in acetone (30 cm^3), and a yellow-tan precipitate formed. The product was filtered off and washed with acetone (10 cm^3), then air dried. Yield: 0.48g; 0.51 mmol; 77%. Found: C, 41.2; H 3.4. Calc. for $C_{32}H_{32}Cl_4Os_2$: C, 40.9; H 3.4%. IR: ν(Os—Cl) 313 (s), 263 (m) cm^{-1}. ^1H NMR (DMSO-d_6): δ 6.90 (s, non-metallated C_6H_4), 5.57 (s, metallated C_6H_4), 2.74 and 3.16 ppm (AA′XX′, $—CH_2CH_2—$). ^{13}C NMR (DMSO-d_6): δ 74.6 (metallated $C_2\mathit{C}_4H_4$), 119.7 (metallated $\mathit{C}_2C_4H_4$), 132.8 (non-metallated $C_2\mathit{C}_4H_4$), 139.3 (non-metallated $\mathit{C}_2C_4H_4$), 31.5 and 32.8 ppm ($—CH_2CH_2—$).

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$ (**3**). $[\{Ru(\eta^6\text{-}C_{16}H_{16})$

$Cl_2\}_2]$ (0.07g; 0.10 mmol) was added to a solution of triphenylphosphine (0.12 g; 0.48 mmol) in toluene (7 cm^3). The mixture was stirred for 2.5 h at room temperature, during which time an orange precipitate formed. The product was filtered off, washed with toluene (5 cm^3) and diethyl ether (5 cm^3), and then air dried. Yield: 0.10 g; 0.15 mmol; 79%. Found: C, 63.0; H, 4.9; Cl, 10.9. Calc. for $C_{34}H_{31}Cl_2PRu$: C, 63.3; H, 5.3; Cl, 11.0%. IR: ν(Ru—Cl) 303 (m), 281 (m); PPh_3 754 (s), 744 (s), 733 (s), 722 (s), 695 (s), 529 (s), 513 (s), 500 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.69 (s, non-metallated C_6H_4), 4.70 (d, metallated C_6H_4; $^3J_{P-H} = 1.1$ Hz), 2.31 and 3.01 (AA′XX′, —CH_2CH_2—), 7.32 (m, 9H) and 7.54 ppm (m, 6H) $[P(C_6H_5)_3]$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.3 ppm (s, PPh_3). MS: *m/z* 642 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]^+$, 607 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)]^+$, 572 $[Ru(\eta^6\text{-}C_{16}H_{16})(PPh_3)]^+$.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PMe_2Ph)]$ (**6**). This compound was prepared by an analogous method to that for **3**. $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (0.06 g; 0.08 mmol) and dimethylphenylphosphine (0.05 cm^3, 0.35 mmol) were used; reaction time 1.75 h. Yield of orange-brown product: 0.05 g; 0.11 mmol; 65%. Found: C, 54.4; H 4.5. Calc. for $C_{24}H_{27}Cl_2PRu$: C, 55.5; H, 5.4%. IR: ν(Ru—Cl) 307 (m), 283 (m); PMe_2Ph 945 (s), 916 (s), 742 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.68 (s, non-metallated C_6H_4), 4.52 (d, metallated C_6H_4; $^3J_{P-H} = 1.6$ Hz), 2.38 and 3.03 (AA′XX′—CH_2CH_2—), 1.68 [d, $P(CH_3)_2$; $^2J_{P-H} = 11.7$ Hz], 7.44 (m, 3H) and 7.70 ppm (m, 2H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.6 ppm (s, PMe_2Ph). MS: *m/z* 518 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PMe_2Ph)]^+$, 483 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)]^+$, 448 $[Ru(\eta^6\text{-}C_{16}H_{16})(PMe_2Ph)]^+$, 346 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl]^+$, 310 $[Ru(\eta^6\text{-}C_{16}H_{16})]^+$.

$[Os(\eta^6\text{-}C_{16}H_{16})Cl_2(PMe_2Ph)]$ (7). This compound was prepared by the method given for **3**. $[\{Os(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (0.06 g; 0.06 mmol) and dimethylphenylphosphine (0.05 cm^3, 0.35 mmol) were used; reaction time 2.5 h. Yield of tan product: 0.03 g; 0.06 mmol; 86%. Found: C, 46.2; H, 4.5. Calc. for $C_{24}H_{27}Cl_2POs$: C, 47.5; H, 4.5%. IR: ν(Os—Cl) 302 (s), 278 (m); PMe_2Ph 944 (s), 915 (s), 741 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.75 (s, non-metallated C_6H_4), 4.88 (d, metallated C_6H_4; $^3J_{P-H} = 1.2$ Hz), 2.36 and 3.05 (AA′XX′, —CH_2CH_2—), 1.71, 1.68 [d, $P(CH_3)_2$; $^2J_{P-H} = 11.4$ Hz], 7.42 (m, 3H) and 7.60 ppm (m, 2H, PC_6H_5).

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)_2][PF_6]$ (**8**). $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (0.08 g; 0.10 mmol) was added to a solution of triphenylphosphine (0.25 g; 0.95 mmol) in methanol (5 cm^3). The mixture was stirred at room temperature for 3 h, giving an orange solution. This was filtered to remove any unreacted starting material and a filtered solution of ammonium hexafluorophosphate in methanol was added to the orange filtrate. This resulted in the rapid precipitation of the yellow microcrystalline product. This was recovered by filtration. Concentration of the filtrate caused further precipitation. The combined precipitates were washed with methanol (5 cm^3), diethyl ether (5 cm^3) and then air dried. Yield: 0.04 g; 0.04 mmol; 19%. Found: C, 60.3; H, 4.9; Cl, 3.4. Calc. for $C_{52}H_{46}ClF_6P_3Ru \cdot 1.5CH_3OH$: C, 60.5; H, 4.9; Cl, 3.3%. IR: ν(Ru—Cl) 295 (w); PPh_3 760 (s), 743 (s), 723 (s), 703 (s), 692 (s), 534 (s), 521 (s), 511 (s), 494 (s); ν(P—F) 848 (s, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.82 (s, non-metallated C_6H_4), 5.18 (br s, metallated C_6H_4), 1.60 and 2.86 (AA′XX′, —CH_2CH_2—), 7.28 ppm (m, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.8 ppm (s, PPh_3). MS: *m/z* 869 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)_2]^+$, 834 $[Ru(\eta^6\text{-}C_{16}H_{16})(PPh_3)_2]^+$, 661 $[RuCl(PPh_3)_2]^+$, 626 $[Ru(PPh_3)_2]^+$, 607 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PPh_3)]^+$, 572 $[Ru(\eta^6\text{-}C_{16}H_{16})(PPh_3)]^+$.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2][PF_6]$ (**9**). This complex was prepared similarly to **8**. $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (0.05 g; 0.07 mmol) and dimethylphenylphosphine (0.10 cm^3, 0.70 mmol) were used; reaction time 3 h. A clear yellow solution formed, to which a filtered solution of ammonium hexafluorophosphate in methanol was added. The solution was kept at *ca* 258 K for 3 days, during which time the orange product precipitated. Yield: 0.05 g; 0.06 mmol; 47%. Found: C, 48.5; H, 4.8; Cl, 4.4. Calc. for $C_{32}H_{37}ClF_6P_3Ru$: C, 50.2; H, 5.0; Cl, 4.6%. IR: ν(Ru—Cl) 289 (w); PMe_2Ph 944 (s), 909 (s), 901 (s), 750 (s), 744 (s); ν(P—F) 840 (s, br) cm^{-1}. ^{1}H NMR. ($CDCl_3$): δ 6.78 (s, non-metallated C_6H_4), 4.95 (br s, metallated C_6H_4), 2.00 and 2.98 (AA′XX′, —CH_2CH_2—), 1.39 and 1.79 [virtual triplets, $P(CH_3)_2$], 7.44 and 7.61 ppm (m, PPh).

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2][BPh_4]$ (**10**). $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl_2\}_2]$ (0.08 g; 0.10 mmol) was added to a solution of dimethylphenylphosphine (0.25 cm^3, 1.75 mmol) in methanol. After 3.5 h an orange solid was isolated from the yellow solution by filtration. The ^{1}H NMR spectrum of this solid revealed it to be $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PMe_2Ph)]$ (**6**). Yield of **6**: 0.04 g; 0.08 mmol; 39%. A solution of tetraphenylboron sodium in methanol was added to the yellow filtrate. A yellow precipitate formed immediately. Yield of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2][BPh_4]$: 0.06 g; 0.06 mmol; 32%. Found: C, 70.4; H, 6.1. Calc. for $C_{56}H_{58}BClP_2Ru$: C, 71.5; H, 6.2%. IR: ν(Ru—Cl) 290 (w); PMe_2Ph 937 (s), 902 (s), 748 (s); $[BPh_4]^-$ 732 (s), 721 (s), 706 (s) cm^{-1}. ^{1}H NMR. (CD_2Cl_2): δ 6.71 (s, non-metallated C_6H_4), 4.67 (br s, metallated C_6H_4), 2.06 and 3.01 (AA′XX′, —CH_2CH_2—), 1.37 and 1.61 [virtual triplets, $P(CH_3)_2$], 7.50 ppm (m, PPh). MS:

m/z: 621 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)_2]^+$, 586 $[Ru(\eta^6\text{-}C_{16}H_{16})(PMe_2Ph)_2]^+$, 483 $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(PMe_2Ph)]^+$, 448 $[Ru(\eta^6\text{-}C_{16}H_{16})(PMe_2Ph)]^+$, 413 $[RuCl(PMe_2Ph)]^+$, 378 $[Ru(PMe_2Ph)_2]^+$.

Crystallography

Details of the crystal structure determination of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]\cdot CHCl_3$ (**3**). *Data collection and reduction*: crystal data for $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]\cdot CHCl_3$ are presented in Table 1. A red crystal was grown by slow evaporation of a chloroform solution of the compound. Initially, the lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 22 reflections ($15° < 2\theta < 27°$) taken from a rotation photograph and located and centred by the diffractometer. A preliminary primitive data set was collected in the range ($20° < 2\theta < 35°$) on a Nicolet R3m/V diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and graphite monochromator. The crystal was recentred on 49 high angle data. Analysis of the data indicated that *C* centring was present, hence reflections where $h+k = (2n+1)$ were omitted from the full data collection. Data were corrected for Lorentz, polarization and absorption effects, using routine procedures. From the systematically absent data the space group was either $C2/c$ or Cc.

Structure solution and refinement: the positions of most of the non-hydrogen atoms were found by direct methods. Iterative application of least-squares refinement and difference-Fourier synthesis led to the development of the entire structure. The refinement of the structure proceeded most smoothly in the higher symmetry space group, $C2/c$, which can thus be regarded as established. The asymmetric unit contains one molecule of the metal complex and one chloroform molecule of crystallization. Hydrogen atoms were included in idealized positions with a fixed isotropic thermal parameter ($U = 0.08$ Å^2). All non-hydrogen atoms were refined anisotropically. Crystallographic calculations used the SHELXTL PLUS program package.[36] Table 2 gives selected bond lengths and bond angles.

Details of the crystal structure determination of $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]\cdot 2CH_2Cl_2$ (**4**). *Data collection and reduction*: crystal data for $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]\cdot 2CH_2Cl_2$ are presented in Table 1. A red crystal was grown by slow evaporation of a dichloromethane solution of the compound. All measurements were made on a Stoe-Siemens diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were refined from 2θ values (23–25°) of 31 reflections measured on both sides of the beam to minimize systematic errors. Data were measured at 160 K by use of a cryostream cooler.[37] Data reduction was carried out with locally written software, and included correction for Lorentz and polarization effects and standard reflection intensity variations; five standard reflections were remeasured every 60 min of X-ray exposure time and varied by up to 3% in intensity. A semi-empirical absorption correction was applied based on sets of equivalent reflections measured at a range of azimuthal angles.[38]

Structure solution and refinement: the programs used in analysis were all members of the SHELX family (SHELXS-86, SHELXL-93 and SHELXTL/PC).[38] From the systematically absent data, the space group was $P2_1/c$. The structure was solved by direct methods, which revealed all of the non-hydrogen atoms. Least-squares refinement was based on F^2 values for all measured reflections except for any flagged for potential systematic errors. Weighted *R* indices (R_w2) are based on F^2 for all data, while $R1$ values are based on F values of "observed" data only (for comparison with conventional refinements based on F). The weighting scheme for the refinement was of the form $w^{-1} = \sigma^2(F_0^2)+(aP)^2+bP$, where $P = (F_0^2+2F_c^2)/3$, F_0^2 being replaced by zero if it is negative. Hydrogen atoms were included in geometrical positions using a riding model. Hydrogen isotropic displacement parameters were set to be 120% of those of the carrier atoms; all other atoms were refined anisotropically. The asymmetric unit comprises one molecule of the metal complex and two dichloromethane molecules of crystallization. Selected bond lengths and bond angles are given in Table 3.

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